

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(19) Japan Patent Office (JP)
(12) Laid-Open Patent Report (A)

(11) Laid-open patent application no. S60-65781

(43) Date laid open: April 15, 1985

(51) IPC:	Identification code:	Internal control no.:
C 04 B 41/83		8216-4G
35/52		7158-4G
H 01 M 8/02		Z-7268-5H

Examination requested: No
Number of inventions: 1

(Total 2 pages)

(54) Title of invention: Impermeable swollen graphite molded body

(21) Patent application no.: S58-173765

(22) Application date: September 20, 1983

(72) Inventor: Yoshihiro KIKUCHI
Sakuragawa Factory, Hitachi Kasei Kogyo Corp., 3-1 Ayukawacho 3-chome,
Hitachi City

(72) Inventor: Kazuo YAMADA
Sakuragawa Factory, Hitachi Kasei Kogyo Corp., 3-1 Ayukawacho 3-chome,
Hitachi City

(72) Inventor: Jun FUJITA
Sakuragawa Factory, Hitachi Kasei Kogyo Corp., 3-1 Ayukawacho 3-chome,
Hitachi City

(71) Applicant: Hitachi Kasei Kogyo Corporation
1-1 Nishi-Shinjuku 2-chome, Shinjuku-ku, Tokyo

(74) Agent: Kunihiko WAKABAYASHI, Patent Attorney

Specification

1. Title of Invention

Impermeable swollen graphite molded body

2. Scope of Patent Claims

1) An impermeable swollen graphite molded body formed by impregnating with resin a molded body of swollen graphite powder or a molded body that was molded by layering said molded bodies, and rinsing away the resin on the surface of the molded body, then heat-curing it.

3. Detailed Explanation of the Invention

This invention pertains to an impermeable swollen graphite molded body. It is applied to fuel cell partition plates and so forth.

The characteristics required of fuel cell partition plates are corrosion resistance against electrolytes, electrical conductivity, and impermeability to air. Corrosion-resistant alloys and carbon materials have been offered as materials that satisfy these requirements. However, all of these have the drawback that materials costs and processing costs are high. For the sake of cost reduction, swollen graphite sheet has been offered as a material that aligns with these goals, but this sheet is corrosive in electrolytes in its direction of thickness, and it has a small volume through which fuel and air pass so that its resistance to passage is large. As a result, there are the problems that supplying fuel is not inexpensive, and constant power is not obtained. Thus, improvements are required.

The purpose of this invention is to provide an impermeable swollen graphite molded body that resolves the aforementioned problems.

This invention pertains to an impermeable swollen graphite molded body formed by impregnating with resin a molded body of swollen graphite powder or a molded body that was molded by layering said molded bodies, and rinsing away the resin on the surface of the molded body, then heat-curing it.

The swollen graphite powder used in this invention is that which has bulk density of about $0.001\text{--}0.02\text{ g/cm}^3$. This swollen graphite powder alone is made into a plate-shape molded body or a bipolar-type grooved molded body of bulk density $0.1\text{--}2.0\text{ g/cm}^3$, preferably $0.5\text{--}1.8\text{ g/cm}^3$, formed by compression-molding by passing it through a press or between rollers, or a plate-shaped molded body or bipolar-type grooved molded body of bulk density $1.5\text{--}2.0\text{ g/cm}^3$, preferably $1.6\text{--}1.8\text{ g/cm}^3$, formed by layering plate-shaped pre-molded bodies molded to bulk density of $0.1\text{--}1.4\text{ g/cm}^3$, and then compression-molding them in a press or between rollers. The plate thickness of the molded body can be suitably selected in the range from about 0.2 cm to several cm.

This molded body is immersed for a time from several minutes to 20 hours in a liquid resin bath whose solid content is at least 10 weight %, and after the molded body surface is rinsed with a solvent, it is heat-cured at $50\text{--}200^\circ\text{C}$. To correct for warping of the molded body during heat-curing, it is preferably cured sandwiched between [illegible] plates.

The amount of resin impregnated in the molded body is adjusted so as to be 0.5–10 weight %, preferably 2–7 weight %. As the resin that is used, a heat-curable resin such as phenol resin, melamine resin, melamine-modified phenol resin, epoxy resin, furan resin and so forth is selected.

Implementation examples are explained below.

Implementation example 1

100 g of Madagascar [illegible] graphite (average 50 mesh) was immersed for 1 hour in a mixed liquid of 300 g of concentrated sulfuric acid and 100 g of concentrated nitric acid, then it was rinsed with water and dehydrated, then it was rapidly heated to 1000°C, and the obtained swollen graphite powder of bulk density 0.005 g/cm³ was compression-molded by being passed between rollers, and a molded body of sheet thickness 0.5 mm and bulk density 1.4 g/cm³ was obtained. Then, this molded body was immersed for 12 hours in melamine-modified phenol resin PR-4060 (trade name, made by Hitachi Kasei Kogyo), and the attached resin on the surface of the molded body was rinsed away with toluene. After that, heat-curing was performed by heating to 160°C at a heating rate of 25°C/hour, and a molded body that was impregnated with 2.5% resin by weight was obtained.

Implementation example 2

Swollen graphite powder of bulk density approximately 0.005 g/cm³ was compression-molded by being passed through rollers, and a molded body of sheet thickness 1.0 cm and bulk density 0.5 g/cm³ was obtained. Several 14 cm × 14 cm tablets were cut from this molded body and layered on top of each other, then molded at a pressure of 800 kg/cm² with a mold that was 14 cm × 14 cm in area, that had protrusions 1 mm high and 1.5 mm wide with a spacing of 3 mm on both surfaces, such that their grids were perpendicular to each other. This grooved molded body was immersed in furan resin VF-303 (trade name, made by Hitachi Kasei Kogyo) for 12 hours, then its surface was rinsed with toluene. Heat-curing was performed in the same way as in implementation example 1. The resin content of this product was 3.2 weight %.

Table 1 shows corrosion resistance in the electrolyte (3 Mol solution of H₂SO₄) and characteristics after resin impregnation for the swollen graphite molded bodies obtained in the implementation examples.

Table 1 Effect of resin impregnation

	Impregnated	Bending strength (kg/cm ²)	Resistivity in direction of thickness (mΩ-cm)	Air permeability (cm ² /s)	Swelling ratio in direction of thickness (%)
Implementation example 1	No	1.2	90	2×10^{-7}	1.3
	Yes	1.8	90	0	0.5
Implementation example 2	No	1.5	75	3×10^{-7}	1.2
	Yes	2.4	75	0	0

As is clear from Table 1, by impregnating with heat-cured resin, the swelling ratio is greatly reduced, air permeability is reduced to zero, and bending strength is increased.

By this invention, by impregnating a swollen graphite molded body with resin, air permeability is greatly improved without losing the electrical characteristics of the swollen graphite molded body, and it becomes impermeable, and mechanical strength is increased, and corrosion in the electrolyte is nearly eliminated.

⑨ 日本国特許庁(JP)

⑩ 特許出願公開

⑪ 公開特許公報(A)

昭60-65781

⑫ Int. Cl.

C 04 B 41/83
35/52
H 01 M 8/02

識別記号

庁内整理番号

8216-4G
7158-4G
Z-7268-5H

⑬ 公開 昭和60年(1985)4月15日

審査請求 未請求 発明の数 1 (全2頁)

⑭ 発明の名称 不透性膨張熱成形体

⑮ 特 願 昭58-173765

⑯ 出 願 昭58(1983)9月20日

⑰ 発 明 者 菊 地 好 洋 日立市鮎川町3丁目3番1号・日立化成工業株式会社鮎川工場内

⑱ 発 明 者 山 田 和 夫 日立市鮎川町3丁目3番1号 日立化成工業株式会社鮎川工場内

⑲ 発 明 者 阪 田 淳 日立市鮎川町3丁目3番1号 日立化成工業株式会社鮎川工場内

⑳ 出 願 人 日立化成工業株式会社 東京都新宿区西新宿2丁目1番1号

㉑ 代 理 人 弁理士 若林 邦彦

明 細 書

1 発明の名称

不透性膨張熱成形体

2 発明の要旨

1 膨張熱成形体の成形体または該成形体を用いて成形した成形体に樹脂を含浸し、成形体の表面の樹脂を脱離除去した後、加熱硬化させてなる不透性膨張熱成形体。

3 発明の詳細を説明

本発明は、不透性膨張熱成形体に関するものであり、その用途は燃料電池用隔壁板などに供されるものである。

燃料電池用隔壁板は、その特性として電解液に対する耐酸性、電気伝導性、且、酸の不透過性が必要とされる。これらの特性を満たす材料として耐酸性合金と炭素材料が提供されている。しかし、いずれも材料費、加工費が高いことが欠点とされている。従来従来のために膨張熱成形シートがこの目的に合う材料として提供されたが、このシートは電解液中で厚み方向に膨張し、燃料、空気の通

路部体積が小さくなり、通過抵抗が大きくなるため燃料の供給が不安定になり、一定出力の電力を得られなくなる問題を生じ、この改善が必要とされていた。

本発明は上記した問題を解決する不透性膨張熱成形体を提供することを目的とする。

本発明は、膨張熱成形体の成形体または該成形体を用いて成形した成形体に、樹脂を含浸し、成形体の表面の樹脂を脱離除去した後、加熱硬化させてなる不透性膨張熱成形体に関する。

本発明で用いる膨張熱成形体は密度 $0.001 \sim 0.02 \text{ g/cm}^3$ 程度のものが用いられる。この膨張熱成形体を単独で、プレスまたはロール間を通して圧縮成形し、密度が $0.1 \sim 2.0 \text{ g/cm}^3$ 好ましくは $0.5 \sim 1.8 \text{ g/cm}^3$ の板状成形体か、パイプタイプの管状成形体とするか、または密度が $0.1 \sim 1.4 \text{ g/cm}^3$ に成形された板状予備成形体を用いて、プレスまたはロール間で圧縮成形し密度 $1.5 \sim 2.0 \text{ g/cm}^3$ 好ましくは $1.6 \sim 1.8 \text{ g/cm}^3$ の板状成形体か、パイプタイプの管状成形体と

する。成形体の板厚は0.2mm程度から数mmまで調整することができる。

この成形体は固形分10重量%以上に調整された溶状樹脂バスマに数分から20時間程度浸漬され、溶剤で成形体表面を洗浄された後、50～200℃で加熱硬化される。加熱硬化の際、成形体の反りを矯正するため、鏡板に接して硬化させることが好ましい。

成形体に含有される樹脂量は0.5～1.0重量%、好ましくは2～7重量%になるよう調整される。使用される樹脂としては、フェノール樹脂、メフミン樹脂、メラミン変性フェノール樹脂、エポキシ樹脂、フラン樹脂などの熱硬化性樹脂が適宜される。

次に実施例を説明する。

実施例1

フタガスカル重質炭黒粉(平均50メッシュ)100gを濃硫酸300gと濃硝酸100gの混合液中1時間浸漬後、水洗、脱水し次いで1000℃に急速加熱して得られる高純度0.005g/cm³の

特開特許60-65781(2)

の炭化炭粉をローン間を通して圧縮成形し板厚0.5mm、高純度1.4g/cm³の成形体を得た。次いでこの成形体をメラミン変性フェノール樹脂PR-4060(日立化成工業製、商標名)中に12時間浸漬し、成形体の表面の付着樹脂をトルエンで洗浄除去した。その後室温から25℃/分で160℃まで昇温して、加熱硬化を行ない高純度2.5g/cm³の樹脂が含有された成形体を得た。

実施例2

高純度の0.005g/cm³の炭化炭粉をローン間を通して圧縮成形し、板厚1.0mm、高純度0.5g/cm³の成形体を得た。その成形体から14cm×14cmの面積で切断したプレートを板厚減薄し、14cm×14cmの面積で両面に減薄1.5mm、高さ1mmの凸状突起を有し、突起間の間隔3mmで互いの導と直交するような成形形状で、面圧300kg/cm²で成形した。その導付成形体をフラン樹脂VP-303(日立化成工業製、商標名)中に12時間浸漬した後、その表面をトルエンで洗浄した。加熱硬化は、実施例1と同条件で行なった。

本品の樹脂含有量は1.2重量%であった。

実施例で得られた炭化炭成形体について、指示液同法の特性および電解液(H₂SO₄の3M溶液)中での電阻値を第1表に示す。

第1表 樹脂含有の効果

	含有率	炭化炭濃度 (g/cm ³)	比抵抗 導み方向 (Ω-cm)	導気率 (Ω ⁻¹ cm)	電阻値 導み方向 (Ω)
実施例1	無	1.2	90	2×10 ⁻⁶	13
	有	1.8	90	0	0.5
実施例2	無	1.5	75	3×10 ⁻¹	12
	有	2.4	75	0	0

第1表から明らかなように、炭化炭樹脂を含有することにより、電阻値が著しく低下し、導気率が著しくなり、電圧降下も増大することがわかる。

本発明によれば炭化炭成形体に樹脂を含有することにより、炭化炭成形体のもつ電気特性を損うことなく、導気率が大幅に改善され、不純物になるとともに、機械的強度が増大し、電解液中での電阻をほとんどなくすることができる。